PATENT SPECIFICATION (11) 1 569 837

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(21) Application No. 36981/77 (22) Filed 5 Sept. 1977
(31) Convention Application No. 26969
(32) Filed 8 Sept. 1976 in
(33) Italy (IT)
(44) Complete Specification published 18 June 1980
(51) INT CL³ C09B 47/04
(52) Index at acceptance
C4P 110 D1T11 D1T15 D1T16 D1T18 D1T33 D1T65 D1T66

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(54) IMPROVEMENTS IN AND RELATING TO PHTHALOCYANINE PIGMENTS

(71) We, AZIENDE COLORI NAZIONALI AFFINI ACNA S.P.A., of Largo Donegani 1/2, 20121 Milano, Italy, an Italian Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to phthalocyanine pigment compositions which exhibit improved characteristics of gloss, transparency and/or fluidity when they are used in solvent inks. The invention also relates to new pigment additives which may be used in preparing the compositions, and to methods of producing the compositions and the additives.

High efficiency organic pigments are often used in fields of application requiring particular properties of gloss and transparency of the pigmented film, these requirements being particularly manifest in the field of the flexographic inks on nitrocellulose and nitrosynthetic bases. Further, for *inter alia* economic reasons, the incorporation of the pigment into the vehicle is desirably effected at a high concentration, as far as is consistent with the rheological requirements of the ink obtained. Therefore, pigments which can be used at high concentrations to give fluid inks are particularly useful.

The present invention permits just these important characteristics of the phthalocyanine pigments to be generally improved. The phthalocyanine may be in the alpha or beta form.

It has already been proposed to use amines of certain types in pigment compositions based on sulphonic derivatives of phthalocyanine (U.S. patent No. 2,187,816; British patents Nos. 1,376,247 and 1,170,895), but we have surprisingly found that it is possible to achieve a considerable improvement of the phthalocyanine pigments' characteristics by employing additives for the pigment compositions based on polyamides or polyamines, which are preferably aliphatic.

The invention consists in an additive for a phthalocyanine pigment which comprises an adduct of a copper phthalocyanine, a copper monochlorphthalocyanine or a mixture of these, in sulphonated form with a polyaminoamido or polyamino compound containing reactive amino groups, i.e. amino groups containing at least one free, and therefore salt-forming hydrogen atom.

The sulphonic derivatives of the phthalocyanine or monochlorphthalocyanine contain one or two $-SO_3H$ groups for each mole of phthalocyanine; a mixture of mono- and di-sulphonated derivatives may be used.

The polyaminoamido or polyamino compound used contains reactive polyamino groups in such amount as to exhibit an amine index of from 100 to 800 mg of KOH per gram of the compound.

Amongst suitable polyaminoamido and polyamino compounds all having an amine index within the above-indicated range there may be mentioned the following commercially available materials:

(a) Genamid (GMI) 250 (Genamid is the trade-mark of General Mills Inc. USA), being a polyamino imidazoline having an amine index of 425—450;
(b) Genamid (GMI) 370, a polyamino-imidazoline having an amine index of 350—400;
(c) Genamid (GMI) 2000, a polyaminoamide having an amine index of 580—620;
(d) Duomeen T (a product distributed by AKZO Chemie) ("Duomeen" is a Registered Trade Mark) a polyamine of formula $H_2N(CH_2)_3NHC_{18}H_{37}$; and
(e) Wolfamids Nos. 3 and 4 ("Wolfamid" is a Registered Trade Mark").

The invention also consists in a pigment composition comprising a copper phthalocyanine or chlorphthalocyanine

pigment or pigment mixture and 5—15% by weight preferably 6—12% by weight, of an adduct as described above.

The adduct may correspond in composition, as regards its phthalocyanine and/or chlorphthalocyanine content, with that of the pigment or pigment mixture, but this is not a necessary feature of the invention.

According to the invention, the pigment composition may be made by mixing the required pigment and adduct components in due proportion. Alternatively it can be made directly by partial sulphonation of the pigment or pigment mixture followed by reaction with the polyaminoamido or polyamino compound of the partially sulphonated material. In yet another alternative these two methods may be combined, in that the polyaminoamido or polyamino compound may be reacted with a mixture of the phthalocyanine pigment material and separately prepared sulphonated phthalocyanine pigment material.

In the direct method, partial sulphonation of phthalocyanine or chlorphthalocyanine pigment may be carried out to an extent giving an intermediate product containing 0.03 to 0.24 equivalents of $-SO_3H$ per mole of phthalocyanine. This intermediate, or an equivalent obtained by mixing an aqueous paste of phthalocyanine $(SO_3H)_{1-2}$ with an aqueous paste of phthalocyanine in the desired ratio, may then be reacted in the form of an aqueous slurry with an aqueous acid solution of the polyamine derivative in the desired ratio. The aqueous slurry may suitably have a pH of 8—9. To promote the reaction the pH may then be adjusted to 3.5—5.5, and the mixture stirred for say 30 minutes to 2 hours at a temperature of from room temperature to 100°C. Finally, the mixture may be filtered and the product washed and dried.

An alternative, as indicated above, consists in preparing the adduct separately, i.e. in reacting the polyamime derivative with the aqueous dispersion of phthalocyanine $(SO_3H)_{1-2}$, and adding the resulting slurry to the aqueous slurry of the not-sulphonated phthalocyanine pigment material.

The following examples illustrate how the invention may be carried into effect.

Example 1.

In a 3-liter beaker, 450 g of an aqueous paste containing 43% by weight of Cu phthalocyanine in the beta form were intensely dispersed in 1500 ml. of hot water, whereupon 120 g of an aqueous paste containing 20% by weight of Cu phthalocyanine monosulphonic acid were added. After becoming a homogeneous slurry, dilute aqueous NaOH was added until the pH was about 9, and then a separately prepared solution of GMI 2000 (10 g) in 60 g of 20% by weight acetic acid was added as well.

Stirring was continued for 1 hour at 70—80°C, after which the slurry was filtered, washed with about 1 liter of water and finally dried.

In comparison with Cu phthalocyanine in the beta form without any additive, the greenish turquoise pigment so obtained exhibited considerably improved fluidity, gloss and transparency in its application in flexographic inks based on nitrocellulose.

Example 2.

In a 3-liter beaker, 250 g of an aqueous paste containing 40% by weight of Cu phthalocyanine in the alpha form and 250 g of an aqueous paste containing 40% by weight of Cu monochloro-phthalocyanine were intensely dispersed in 1500 ml. of hot water, and 80 g of an aqueous paste containing 20% by weight of Cu phthalocyanine monosulphonic acid were then added.

After the slurry mixture was stirred to homogeneity, dilute aqueous NaOH was added to adjust the pH to about 9, and a separately prepared solution of 10 g of GMI 2000 in 50 g of 20% acetic acid was then poured in.

The mixture was then worked up as in Example 1, to give a washed and dried product exhibiting a reddish turquoise shade. In comparison with a similar mixture of phthalocyanines, but not containing the additive of the present invention, the product of Example 2 exhibited an improved fluidity, gloss and transparency in application to flexographic inks on a nitrocellulose basis.

Example 3.

In a 3-liter beaker, 450 g of an aqueous paste containing 43% by weight of Cu phthalocyanine in the beta form were intensely dispersed in 1500 ml. of hot water, and 120 g of an aqueous paste containing 20% by weight of Cu phthalocyanine monosulphonic acid were then added.

After the resulting slurry mixture became homogeneous, a separately prepared solution of Duomeen T acetate (10 g) in 50 g of 70% w/w acetic acid was added. Stirring was continued for 1 hour at 70—80°C, after which the slurry was filtered, washed with about 1 liter of water and finally dried.

As compared with beta Cu phthalocyanine without any additive, the pigment so obtained exhibited considerable improvements as regards fluidity, gloss and transparency in its application in

flexographic inks based on nitrocellulose.

Example 4.

In a 3-liter beaker, 450 g of an aqueous paste containing 43% by weight of beta Cu phthalocyanine were intensely dispersed in 1500 ml. of hot water.

In a second 500 ml. beaker, 50 g of a paste containing 20% by weight of Cu phthalocyanine monosulphonic acid were dispersed in 200 ml. of hot water, then the pH was brought to 9 with dilute NaOH, whereupon a separately prepared solution of 2.5 g of GMI 2000 in 15 g of 20% w/w acetic acid was added. Stirring was continued for 1 hour keeping the temperature at 80°C, whereupon the dispersion was poured into the first beaker. The mixture was stirred intensely for about 30 minutes, then it was filtered, washed with about 1 liter of water and finally dried. The resulting product exhibited practically the same characteristics as that described in Example 1.

WHAT WE CLAIM IS:—

1. An additive for phthalocyanine pigments comprising an adduct of a copper phthalocyanine mono or disulphonic acid and/or of the corresponding monochloro-derivative with a polyaminoamido or polyamino compound having an amine index of from 100 to 800 mg of KOH per gram.

2. An additive according to claim 1 in which said compound is aliphatic.

3. A pigment composition comprising a copper phthalocyanine or chlorphthalocyanine pigment or pigment mixture and 5—15% by weight of an adduct according to claim 1 or 2.

4. A composition according to claim 3 in which 6—12% by weight of the adduct is present.

5. A process for preparing a pigment composition according to claim 3 or 4 in which the pigment or pigment mixture is compounded with the separately-prepared adduct.

6. A process according to claim 5 in which the pigment or pigment mixture and the adduct are each in the form of an aqueous dispersion and they are compounded by being stirred together at an acid pH.

7. A process for preparing a pigment composition according to claim 3 or 4 in which a mixture of the corresponding sulphonated and unsulphonated phthalocyanines and/or chlorphthalocyanines is reacted in the form of an aqueous dispersion with the polyaminoamido or polyamino compound.

8. A process according to claim 7 in which said mixture is obtained by partial sulphonation of the corresponding phthalocyanine and/or chlorphthalocyanine.

9. A process of preparing a pigment composition according to claim 3 or 4, substantially as exemplified.

10. Solvent inks comprising a pigment composition according to claim 3 or 4, or produced according to any of claims 5—9.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1980.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.